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REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION	1b. RESTRICTIVE MARKINGS
Unclassified	

2a. SECURITY CLASSIFICATION AUTHORITY	3. DISTRIBUTION / AVAILABILITY OF REPORT
	Approved for public release
2b. DECLASSIFICATION / DOWNGRADING SCHEDULE	Distribution unlimited

4. PERFORMING ORGANIZATION REPORT NUMBER(S)	5. MONITORING ORGANIZATION REPORT NUMBER(S)
AD-A200 331	AFOSR-TR- 88-1113

6a. NAME OF PERFORMING ORGANIZATION	6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION
University of California at Berkeley		AFOSR/NC

6c. ADDRESS (City, State, and ZIP Code)	7b. ADDRESS (City, State, and ZIP Code)
Berkeley, California 94720	Bldg. 410 Bolling Air Force Base Washington, D.C. 20332-6448

8a. NAME OF FUNDING / SPONSORING ORGANIZATION	8b. OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER
AFOSR	NC	AFOSR-87-0182

8c. ADDRESS (City, State, and ZIP Code)	10. SOURCE OF FUNDING NUMBERS			
Bldg. 410 Bolling Air Force Base Washington, D.C. 20332-6448	PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.	WORK UNIT ACCESSION NO.
	61102F	2303	B3	

11. TITLE (Include Security Classification)

Fundamental Studies of Carbon, NH, and Oxygen Rings and Other High Energy Density Molecular Systems

12. PERSONAL AUTHOR(S)

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13a. TYPE OF REPORT	13b. TIME COVERED	14. DATE OF REPORT (Year, Month, Day)	15. PAGE COUNT
Final	FROM 4/1/87 TO 3/31/88	August 30, 1988	

16. SUPPLEMENTARY NOTATION

17.	COSATI CODES		18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB-GROUP	Ab initio, computational chemistry, quantum chemistry, theoretical chemistry, propellants.

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

The object of this research was the characteriztion of the molecular structures, energetics, and spectroscopic properties of the oxygen ring molecules O_4 and O_6.

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OCT 1 3 1988
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20. DISTRIBUTION / AVAILABILITY OF ABSTRACT	21. ABSTRACT SECURITY CLASSIFICATION
☒UNCLASSIFIED/UNLIMITED ☒SAME AS RPT ☐DTIC USERS	Unclassified

22a. NAME OF RESPONSIBLE INDIVIDUAL	22b. TELEPHONE (Include Area Code)	22c. OFFICE SYMBOL
Major Larry P. Davis	(202)767-4963	NC

DD FORM 1473, 84 MAR
83 APR edition may be used until exhausted.
All other editions are obsolete.

88 1011

FINAL REPORT
AFOSR-87-0182

Henry F. Schaefer III

Fundamental Studies of Carbon, NH, and Oxygen Rings and Other High Energy Density Molecular Systems

The development of efficient and safe conventional (i.e., nonnuclear) propellants and/or fuels is a goal of obvious technological significance. A desirable quality of such a propellant is clearly a high ratio of energy release to mass. The present hypothesis rests on a simple, but previously unrecognized, analogy between oxygen and sulfur. Preliminary studies showed that the oxygen ring systems are sufficiently promising to warrant the detailed, high-level theoretical research reported here.

Our idea begins with the observation that elemental sulfur exists as sulfur rings, S_n. The stability of these sulfur rings is attested by the fact that the single most important commercial source of sulfur is elemental sulfur in the caprock salt domes in the United States and Mexico. The most common allotrope of sulfur is the yellow, orthorhombic α form, to which all other modifications eventually revert at room temperature. As long ago as 1935 the crown structure of cyclo-S_8 was established by x-ray crystallography. The D_{4d} point group experimental structure of S_8 is widely known.

The essence of our proposal is to make an analogy between sulfur rings and oxygen rings. Given the remarkable stability of sulfur rings, should it not be possible to prepare oxygen rings? Oxygen lies directly above sulfur in the Periodic Table, and the analogy is an appealing one. Before pressing on further with this analogy, let us say a bit more about cyclic forms of sulfur other than S_8.

Although S_8 dominates elemental sulfur, more than a dozen additional sulfur rings S_n have been synthesized in the past 20 years. Long before this, in 1891, a rhombohedral form, ϵ-sulfur, was prepared by Engel. By 1961 ϵ-sulfur was clearly established to be cyclo-S_6. Note that for both S_6 and S_8 all sulfur atoms are equivalent. S_7 is alos known to exist as a C_s ring structure, with four distinct S-S distances, ranging from 1.99 to 2.18 Å S_{11}, and S_{13} have been synthesized and appear from spectroscopic studies to be cyclic, although no crystal structures have been reported.

S_{10} belongs to the rarely observed point group D_2 and has experimental bond distances in the relatively narrow range 2.03 - 2.08 Å The 12 membered sulfur ring was predicted in 1949 in a classic paper by Pauling to be unstable. Nevertheless, S_{12} was synthesized in 1966 and turns out to be second only to S_8 in stability. S_{12} is monocyclic, with S-S bond distances in the very narrow range 2.05 - 2.06 Å S_{18} is also monocyclic, as is S_{20} and experimental cyrstal structures exist for both molecules.

1

The reason for this relatively detailed description of the cyclic S_n isomers is that there should be a one-to-one correspondence with cyclic O_n isomers, a principal topic of this research. However, unlike the S_n sulfur rings, the analogous O_n rings will be high energy density molecular systems.

Before going on further, let us attempt to make some plausible guesses as to the energy content of the metastable O_n rings. First one notes that the valence-isoelectronic cyclic S_8 contains *no* energy in this sense. Specifically, crystalline S_8 lies 15.4 ± 0.1 kcal per mol of sulfur atoms below four gas phase diatomic S_2 molecules. Can one guess thsi result using the dissociation energy of S_2 ($D_0 = 4.37$ eV $= 100.8$ kcal/mol) and some reasonably standard S-S single-bond dissociation energy, say 54 kcal/mol? The answer to this question is a qualified "yes". Using this simple model, one predicts S_8 to lie $(54 - 50.4) = 3.6$ kcal/mol below four S_2 molecules on a per atom basis. By increasing the S-S bond energy from the standard 54 to 66 kcal, the known experimental energy difference for

$$S_8 (\text{crystalline}) \rightarrow S_2 \qquad\qquad 1$$

is precisely reproduced. This adjustment reflects the fact that the S-S bonds in S_8 are stronger than those in organosulfur compounds such as CH_3SSCH_3.

The comparable oxygen thermodynamic data make it immediately obvious why oxygen rings should be high energy density materials. First the standard O-O bond dissociation strength is 35 kcal/mol, *much weaker* than the 54 kcal for S-S bonds. Second, the dissociation energy of diatomic O_2 is $D_0 = 5.12$ eV $= 118.0$ kcal/mol, *much stronger* than the 100.8 kcal for S_2. Thus, the estimate for the energy stored in the "generic" oxygen ring is $(35-59_- = -24$ kcal per mole of oxygen atoms. That is, the dissociation process
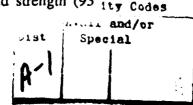
$$O_n \ (\text{n even}) \rightarrow \frac{n}{2} \ O_2 \ (\text{g}) \qquad\qquad 2$$

is estimated to be exothermic by 24 kcal per mole of oxygen atoms. Alternately 48 kcal *of energy is released per mole* of O_2 molecules. A *larger* energy release might be expected for the smaller rings, specifically O_4 and O_6, which presumably have smaller average O-O bond energies due to ring strain.

A similar estimate is readily made for the isoelectronic cyclic system $(NH)_n$, which will also be metastable and dissociate (directly or indirectly) via

$$(NH)_n \ (\text{n even}) \rightarrow \frac{n}{2} \ (\text{g}) + \frac{n}{2} \ H_2 \ (\text{g}). \qquad\qquad 3$$

This proposal, of course, takes advantage of the tremendous strength ($D_0 = 9.76$ eV $= 255.1$ kcal/mol) of the N≡N triple bond. Using in addition $D_0(H_2) = 4.48$ eV $= 103.3$ kcal and the average N-N single bond strength (39 kcal) and N-H bond strength (93

$$39 + 93 - 112.5 - 51.6 = -32.1 \text{ kcal}$$

per mole of N (or H) atoms. Alternately, reaction (3) is suggested to be exothermic by 64.2 kcal/mol of N_2 molecules releases. It is apparent that within the limits of the simple estimates made here, systems like $(NH)_8$ may be even more effective than the above-discussed oxygen rings as high energy density molecular systems. It is ultimately intended to theoretically investigate both O_n and $(NH)_n$. The order of the discussion presented above was mandated by the analogy (with the sulfur rings) by which this idea came to us.

A traditional measure of the effectiveness of a propellant is the specific impulse I_{sp}. I_{sp} is given in seconds from the relationship

$$I_{sp} = (\text{constant})\frac{\Delta H(\text{kcal/mol})}{\text{Molecular weight}(\text{g/mol})}.$$

The traditional standard of comparison is the exothermic reaction

$$H_2 + \tfrac{1}{2}O_2 \rightarrow H_2O \qquad\qquad 4$$

for which I_{sp} is on the order of 400 s. Substitution of unstrained (e.g., O_8) oxygen rings for O_2 will increase the specific impulse by ~100 s. Use of the smaller oxygen rings O_4, O_5, or O_6 would presumably result in a significantly larger I_{sp}.

It should be emphasized of course that high energy density is a necessary but certainly not sufficient condition for the development of an effective propellant. The material also must have a significant range of metastability - it should not explode when a match is unintentionally lit 100 m away. The great stability of elemental sulfur, in the form of sulfur rings, gives some encouragement that the band of metastability for oxygen and NH rings might be rather broad. Precisely this point, of course, may be investigated in the theoretical studies of the type reported here.

Due to the weakness of the O-O single bonds, as in hydrogen peroxide, it is hypothesized that oxygen rings are potential high energy density materials. A particularly attractive candidate is the O_4 molecule, for which ring strain is expected to provide further destabilization relative to two separated O_2 molecules. To pursue these qualitative suggestions, *ab initio* molecular quantum mechanics has been employed. Both self-consistent field (SCF) and configuration interaction including single and double excitations (CISD) methods have been employed in conjuction with double zeta plus polarization basis sets. At the highest level of theory the nonplanar (D_{2d} point group, O-O-O-O torsional angle 25 °) equilibrium structure is predicted to lie 2.9 kcal below the planar D_{4h} structure, which is a transition state. The infrared spectrum is predicted at the DZ + P CISD level, as well as lower levels of theory. The O_4 minimum is predicted to lie ~ 100 kcal/mol above the asymptotic limit of two O_2 molecules.

Self-consistent field (SCF) methods with minimum (STO-3G), double ζ (DZ), and double ζ plus polarization (DZP) basis sets predict the O_6 ring to assume chair, twist,

Self-consistent field (SCF) methods with minimum (STO-3G), double ζ (DZ), and double ζ plus polarization (DZP) basis sets predict the O_6 ring to assume chair, twist, and boat conformations analogous to similar forms for cyclohexane. All predicted vibrational frequencies for the chair and twist forms are real. Six symmetrically equivalent oxygen atoms are predicted to comprise the lowest energy chair form, with O-O bond distances of 1.364 Å and bond angles of 104.7° at the DZP SCF level of theory. The boat form is not found to be an energy minimum but rather exhibits one imaginary vibrational frequency which when followed tends toward assumption of the twist form. Energy differences at the DZP SCF level are computed to be 15.9 kcal between the chair and twist forms and 17.5 kcal between the chair and boat. We interpret these results by analogy with cyclohexane and assign the larger energetic discrepancies to shorter bond distances and inherently greater eclipsing effects for adjacent lone electron pairs than those attributed to bonding electron pairs. Homodesmotic and hyperhomodesmotic reactions devised to predict the decomposition exothermicity of the ring give rather different results, namely, ~130 (homodesmotic) and ~75 (hyperhomodesmotic) for the heat for formation of O_6. Higher level theoretical studies will be required to resolve this energetic discrepancy.